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# Electrochemical Deposition and Characterization of Hydroxyapatite (HAp) on Titanium Substrate

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## Abstract

Hydroxyapatite (HAp) coatings were successfully prepared onto titanium substrate by electrodeposition technique. XRD pattern and FTIR spectrum confirmed that pure hydroxyapatite crystals were deposited onto the titanium surface. Newly formed HAp crystals can grow on the as-deposited HAp coatings by immersion in SBF solution. The surface morphology of the HAp coatings has significantly changed with immersion time in the SBF solution.

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*Keywords:* Hydroxyapatite, Electrodeposition, Bioactivity, Simulated Body Fluid (SBF)

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## 1. Introduction

Hydroxyapatite (HAp) is an important material for biomedical implants, as its chemical composition is similar to natural bone [1]. Synthetic HAp has been commonly used as a coating material for metallic implants due to its biocompatibility and ability to form strong bonds with bones. However, its mechanical properties of low strength and high brittleness restrict the application only for bone repair [2]. Therefore, combining the HAp with high strength and toughness of metals should be a good idea. Conventionally, plasma spray has been successfully used in the fabrication of HAp coated titanium (Ti) substrate [3-4]. However, the plasma sprayed HAp has a disadvantage of possessing low bonding strength at coatings/implant interface. The strength decreases over time in simulated body fluid (SBF) solution which is attributed to its

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low crystallinity and microcracks formation due to high-temperature process [1]. Since the processing temperature is high, the coatings might contain various HAp phases such as melted and crystallized HAp, unmelted HAp, amorphous phase and some decomposed phases [5].

In order to avoid the disadvantage of the plasma spray, electrodeposition is an alternative technique to be considered to coat HAp on Ti substrate [6-7]. This process could be carried out under a mild experimental condition which is at relatively lower temperature so that unwanted phase changes could be avoided. This method also produces highly crystalline coatings with low solubility in body fluids and low residual stresses.

There is a great interest in understanding the electrochemical process of HAp deposition on the Ti substrate by studying the current peak appeared in cyclic voltammogram. It is important to identify a suitable applied potential for electrodeposition of HAp in order to produce good coatings without the interference of H<sub>2</sub> evolution.

In this study, the possibility of depositing HAp coatings on Ti substrate by electrodeposition process was investigated. The surface morphology, crystallography and chemical composition of the HAp coatings were characterized using FESEM, XRD and FTIR, respectively. The bioactivity of the HAp coatings immersed in SBF solution for several days was also observed by FESEM.

## 2. Experimental

### 2.1. Substrate pre-treatment

Prior to electrodeposition, the Ti substrates were etched in 12 M HCl at 80 °C for 1 h in order to remove oxide and to increase the roughness of the substrates for better adhesion. After the etching process, the specimens were washed with distilled water and dried before further coatings process.

### 2.2. Electrodeposition of HAp coatings

The electrodeposition of HAp onto etched Ti substrates was carried out in a typical three-electrochemical cell. The etched Ti substrate was used as working electrode and acted as cathode in the process. A Pt foil was used as counter electrode (anode) and a standard Ag/AgCl as reference electrode. The electrodeposition was controlled using an Autolab Potentiostat (Aut302 FRA2). The deposition solution contained 0.167 M CaCl<sub>2</sub> and 0.1 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> with Ca/P ratio being 1.67 in distilled water. 0.1 M NaCl was added in order to improve the conductivity of the electrolyte. The pH of the solution was adjusted to 6.0 by adding NaOH and measured by Mettler Toledo pH meter. The temperature was controlled at 80 °C for 30 min under constant potential at –1.5 V vs Ag/AgCl during electrodeposition process. After the electrochemical deposition of coatings, the coated substrate was rinsed with distilled water and dried at room temperature in air.

### 2.3. Characterization of HAp coatings

The crystallinity and structure of the coatings were examined using diffractometer (X'pert pro-MPD, PANalytical) with thin-film X-ray diffraction (TF-XRD). The morphology of the coatings was examined using Field Emission Scanning Electron Microscopy (FESEM, Carl Zeiss SMT Supra 40VP). The chemical composition of the coatings was analyzed using Fourier Transform infrared spectroscopy (FTIR, Perkin Elmer 1725x). In order to evaluate bioactivity of the coatings, the coated substrate was immersed in 20 ml of SBF solution with ion concentrations similar to that of human blood plasma at 36.5 °C for several days. The SBF solution was prepared as described by Kokubo & Takadama, 2006 [8].

### 3. Results and discussion

In electrochemistry process, the nature of electrode reactions can often be determined based on the peak current in cyclic voltammetry (CV). Thus, electrochemical synthesis of HAp was performed by cyclic voltammetry (CV) to determine the reduction peaks occurring during the deposition process of HAp on Ti substrate. Fig. 1a presents a cyclic voltammogram of etched Ti substrate that was performed in a typical three-electrode electrochemical cell over a range of 0 V to -3.0 V, with 100 mV/s scanning rate at 80 °C in a solution containing 0.167 M CaCl<sub>2</sub> + 0.1 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> + 0.1 M NaCl. From the cyclic voltammogram, it was observed that the electrochemical reaction of electroactive species in the bath solution started to occur at about -0.7 V.

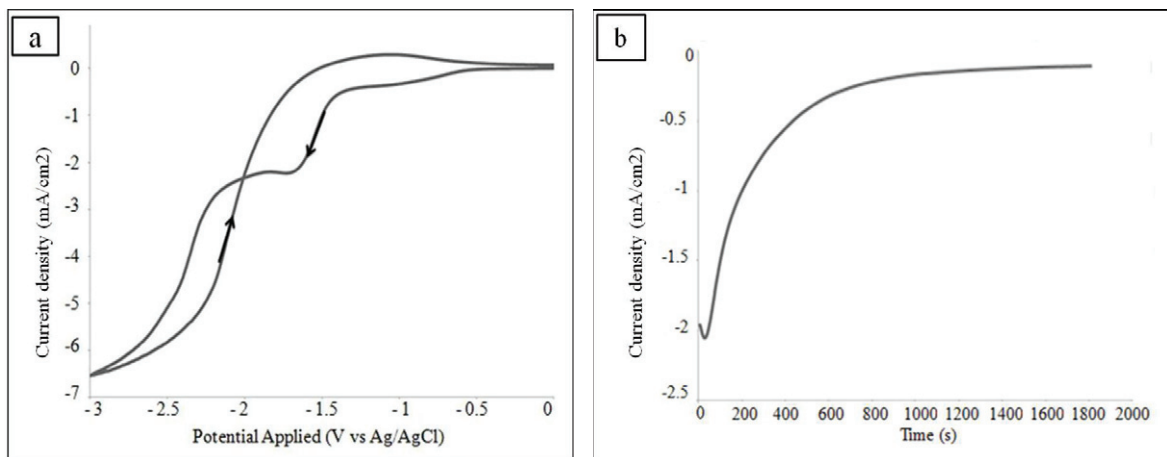


Fig. 1. (a) Cyclic voltammogram of etched Ti substrate in 0.167 M CaCl<sub>2</sub> + 0.1 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> + 0.1 M NaCl solution at 80 °C. Scan rate: 100 mV/s; (b) Chronoamperometry plot of electrodeposition process of HAp on Ti substrate from 0.167 M CaCl<sub>2</sub> + 0.1 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> + 0.1 M NaCl solution at 80 °C by applying constant potential of -1.5 V vs Ag/AgCl for 30 min.

The current density slowly increased between -0.7 V until -1.4 V indicating the nucleation process of HAp particles on Ti surface and the process was controlled by electron transfer. A drastic increase of current density was observed between -1.4 V until -1.6 V which corresponds to the deposition of HAp and it was controlled by a mixed process of electron transfer and mass transport. A plateau of current density was observed from -1.6 V to -2.2 V corresponding to the mass transport controlled process. The evolution of hydrogen was the dominant reaction at potential > -2.2 V which a lot of bubbles were observed at the Ti surface during the scanning. From these findings, it can be concluded that the desirable potential range for the electrodeposition of good HAp coatings on the Ti substrate without the interference of hydrogen evolution is between -0.7 V to -2.2 V. In this study, the value of -1.5 V is used as the potential for potentiostatic deposition of HAp on the Ti substrate.

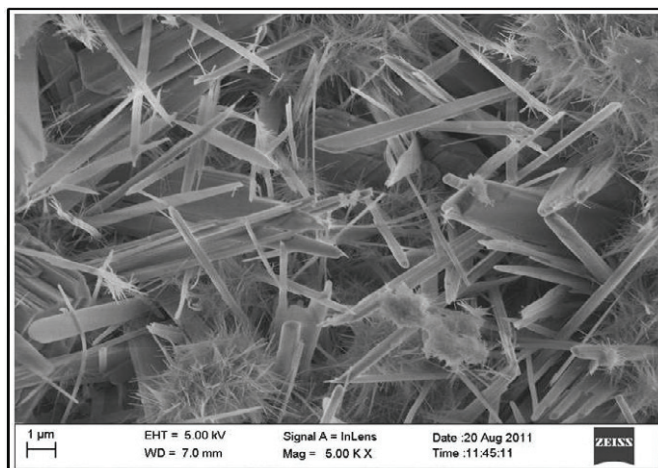


Fig. 2. SEM image of HAp coatings electrodeposited on Ti substrate by applying constant potential of -1.5 V vs Ag/AgCl for 30 min at 80 °C from 0.167 M CaCl<sub>2</sub> + 0.1 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution.

Fig. 1b exhibits current behaviour of HAp deposited onto Ti substrate during potentiostatic deposition at -1.5 V for 30 min. This continuous curve can be divided into three periods. Initially, a quick drop of current density (i.e.: the first 12 s) indicates the charging of double layer or the fast formation of barrier calcium phosphate layer onto Ti surface. The second period (i.e.: >12 s to 1200 s) shows the drastic increase of current density due to the nucleation step corresponding to the creation of active sites at the Ti surface. Finally, a constant value of current density is reached after 1200 s corresponding to the growth of the HAp at the Ti surface is under the same deposition rate. The morphology of the coatings can be clearly observed from an SEM image as shown in Fig. 2. The coating appears in the mixture of needle-like crystals with various diameter sizes ranging from around 50 nm – 520 nm.

Fig. 3 shows the XRD patterns of the etched Ti substrate (Fig. 3a) and the HAp coatings formed onto the etched Ti substrate after electrodeposition process at -1.5 V (vs Ag/AgCl) for 30 min (Fig. 3b). It shows that all reflections can be indexed readily to the standard HAp patterns and Ti. The appearance of Ti reflections existing in Fig. 3b indicates that the coatings deposited on the Ti substrate should be quite thin. The indexed calculations reveal that the deposited material has a hexagonal HAp structure with unit cell parameters calculated from the XRD pattern of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> (a = b = 9.352 Å and c = 6.882 Å) obtained from ICSD database reference pattern HAp 01-086-0740. The most intense and sharp lines are observed in the 2θ angle range between 25° and 60°. These lines are coincident with lines of the XRD pattern of reference, which corresponds to pure HAp crystals. From the XRD pattern as in Fig. 3b, it indicates that pure HAp crystals were produced on Ti surface by the electrodeposition process when taking no account of the Ti peaks. The peak related to the (002) plane from HAp (2θ = 25.9°) indicates that the HAp crystals are gradually oriented along c-axis during the growth of HAp coating on Ti surface.

Fig. 4 shows the FTIR spectrum of the powders scratched from the coating formed on the Ti surface which exhibiting typical characteristics of the HAp crystals. It can be seen that bands corresponding to the absorption peaks of OH<sup>-</sup> groups appeared at around 3447 cm<sup>-1</sup> and 1645 cm<sup>-1</sup>. The vibrational bands of 566 – 1022 cm<sup>-1</sup> are mainly attributed to PO<sub>4</sub><sup>3-</sup> absorption peaks. Broad stretching bands at 3447 cm<sup>-1</sup> as well as bending band at 1645 cm<sup>-1</sup> for absorbed OH<sup>-</sup> group are considered as characteristics of the HAp phase. The absorption peaks in the sample due to PO<sub>4</sub><sup>3-</sup> and OH<sup>-</sup> show strong intensities in the spectrum. These peaks are the signature peaks of HAp. This FTIR result is in a good agreement with XRD analysis.

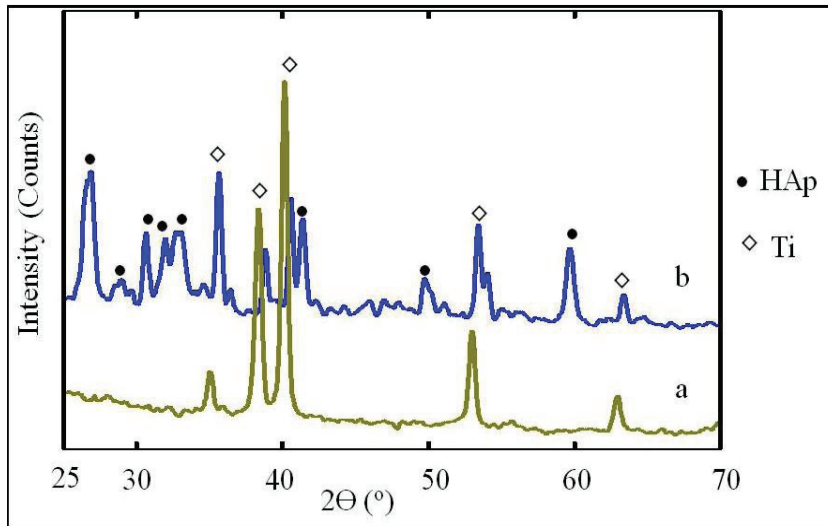


Fig. 3. XRD patterns of the (a) etched Ti substrate; (b) HAp coatings formed on the Ti substrate after electrodeposition process from solution containing 0.167 M  $\text{CaCl}_2$  and 0.1 M  $\text{NH}_4\text{H}_2\text{PO}_4$  at  $-1.5$  V (vs Ag/AgCl) for 30 min.

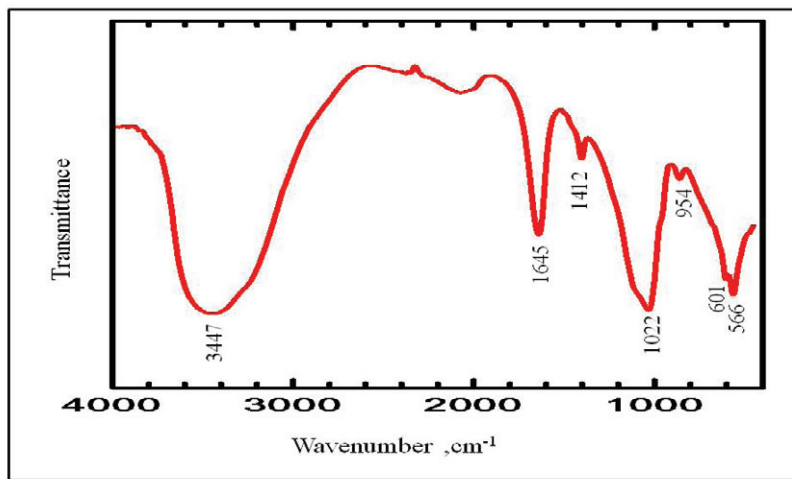


Fig. 4. FTIR spectrum of coatings electrodeposited at  $-1.5$  V vs Ag/AgCl from 0.167 M  $\text{CaCl}_2$  + 0.1 M  $\text{NH}_4\text{H}_2\text{PO}_4$  at  $80^\circ\text{C}$  for 30 min.

Fig. 5 shows the SEM images of the HAp coatings electrodeposited on Ti substrate after subsequent immersion in the SBF solution for 1 day (Fig. 5a), 4 days (Fig. 5b) and 7 days (Fig. 5c). It can be seen clearly in Fig. 5a, the surface of the HAp coatings after immersion in SBF solution for 1 day has slightly modified as compared to as-deposited HAp coating as shown earlier in Fig. 2. Newly formed crystals appeared on the coatings surface which appropriate to the apatite crystals. After 4 days of immersion, the morphology of the

coating surface has significantly changed to chip-shape crystals as shown in Fig. 5b. The homogeneous chip-shape crystals are completely covered the entire coating surface. Meanwhile, after 7 days immersion, similar chip-shape crystals as 4 days immersion were observed but the coatings were more compact and denser which uniformly distributed all over the coating area as in Fig. 5c. This morphology is similar to that previous image reported by kokubo and Takadama, 2006 [8].

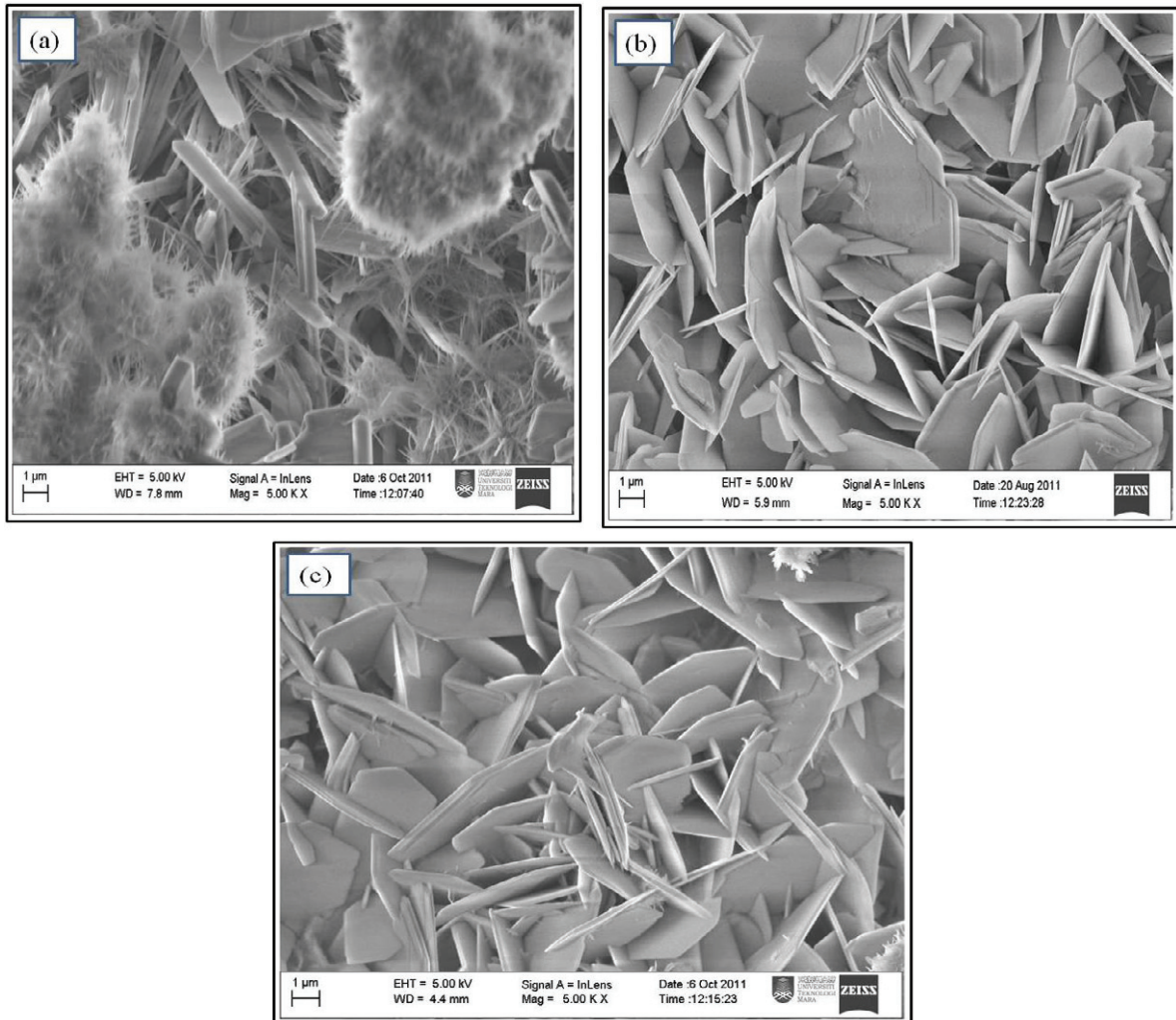


Fig. 5. SEM images of the HAp coatings after immersion in SBF solution for (a) 1 day; (b) 4 days and (c) 7 days.

#### 4. Conclusion

HAp coatings were successfully deposited on Ti substrate by electrodeposition technique. XRD patterns and FTIR spectrum confirmed that the coatings consist of HAp crystals. The surface morphology of the HAp coatings has significantly changed after immersion for several days in SBF solution as observed by FESEM. It can be concluded that the prepared HAp is bioactive by forming new apatite crystals when immersed in

SBF solution.

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